Supporting Information For

Are Bidentate Ligands Really Better than Monodentate Ligands On Nanoparticles?

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Mass Spectra of dye before and after modification according to Scheme 1.

MALDI-TOF mass spectra of the as-purchased Atto700-amine and the resulting thiolated dye were acquired on a Bruker UltraflexII Mass Spectrometer (Figure S1(a) and (b), respectively). Successful thiolation of the dye was verified by the higher mass peaks corresponding to the dye + SATA (Figure S1(b), which came off the C-18 HPLC column at a longer retention time as shown in figure 1 of the main text.

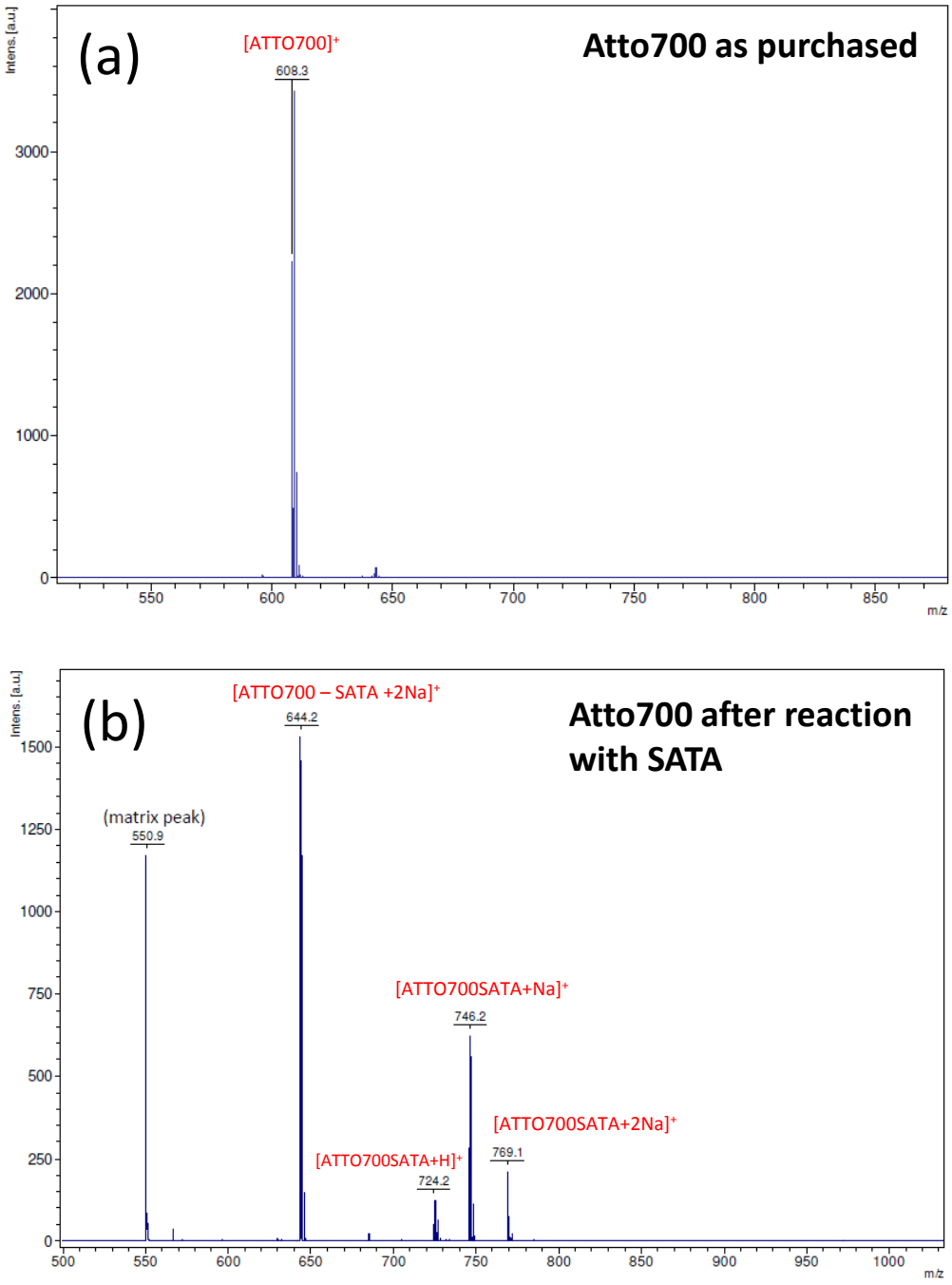

Figure S1

Absorption and PL spectra of the original QDs, MPA-QDs and DHLA-QDs with thin and thick shells.

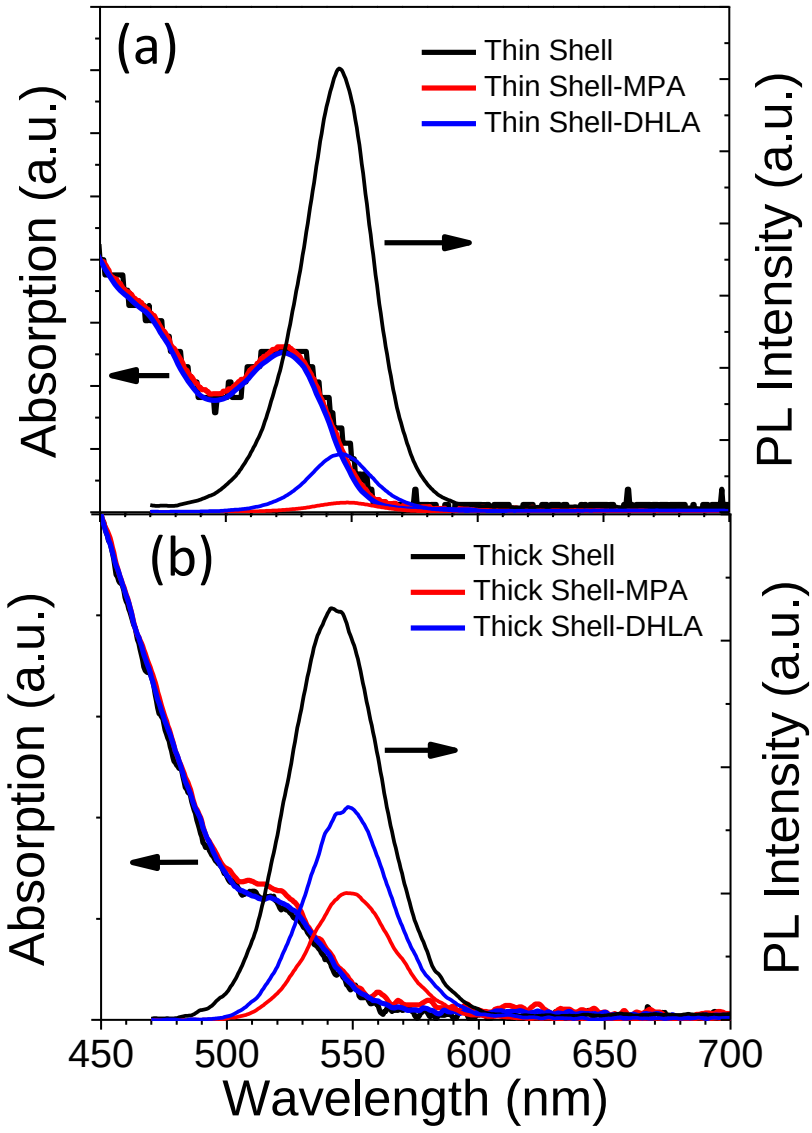

Figure S2

Trap emission from some batches of thin-shell QDs

We purchased several batches of core-shell CdSe-ZnS QDs from two different companies; NNLabs, Fayetteville, AR and Ocean Nanotech, Springdale, AR. We purchased their 'standard' 520 nm emitting samples, which were found by TEM to have ~3ML of ZnS shell. We also requested thick-shell QDs as a

special order. The ability for thin-shell QDs to undergo ligand exchange without detrimental effects on their emission varied from batch-to-batch, with some samples showing spectra similar to Figure S3. Samples that showed this trap emission problem were not used for further study.

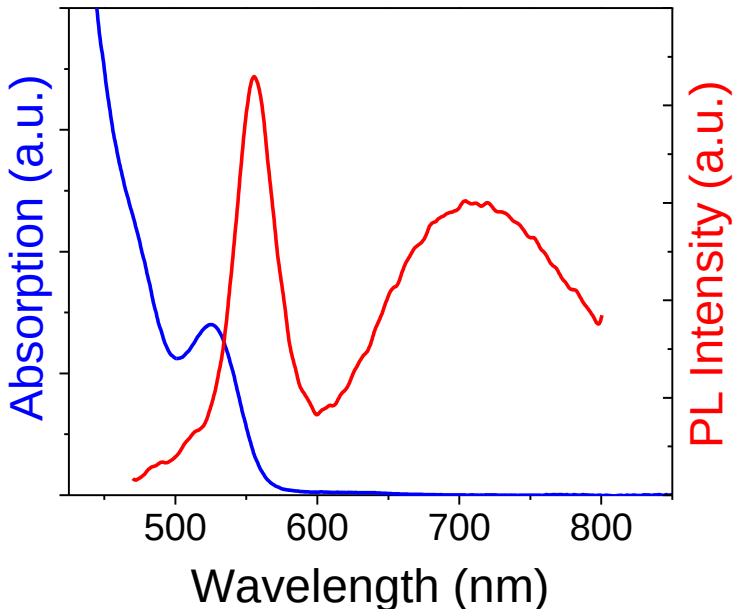

Figure S3

Size exclusion chromatography of QD-dye conjugates

Efficient separation of QD and QD-dye conjugates from free dye was accomplished by size exclusion chromatography, as depicted in figure S4(a). Example chromatograms for DHLA-QD:added dye ratios of 1:2 and 1:100 are shown in Figure S4(b) and (c), respectively. Even when large amounts of free dye are present, efficient separation is possible, ensuring that the resulting absorption and emission spectra are representative of QD-dye conjugates only.

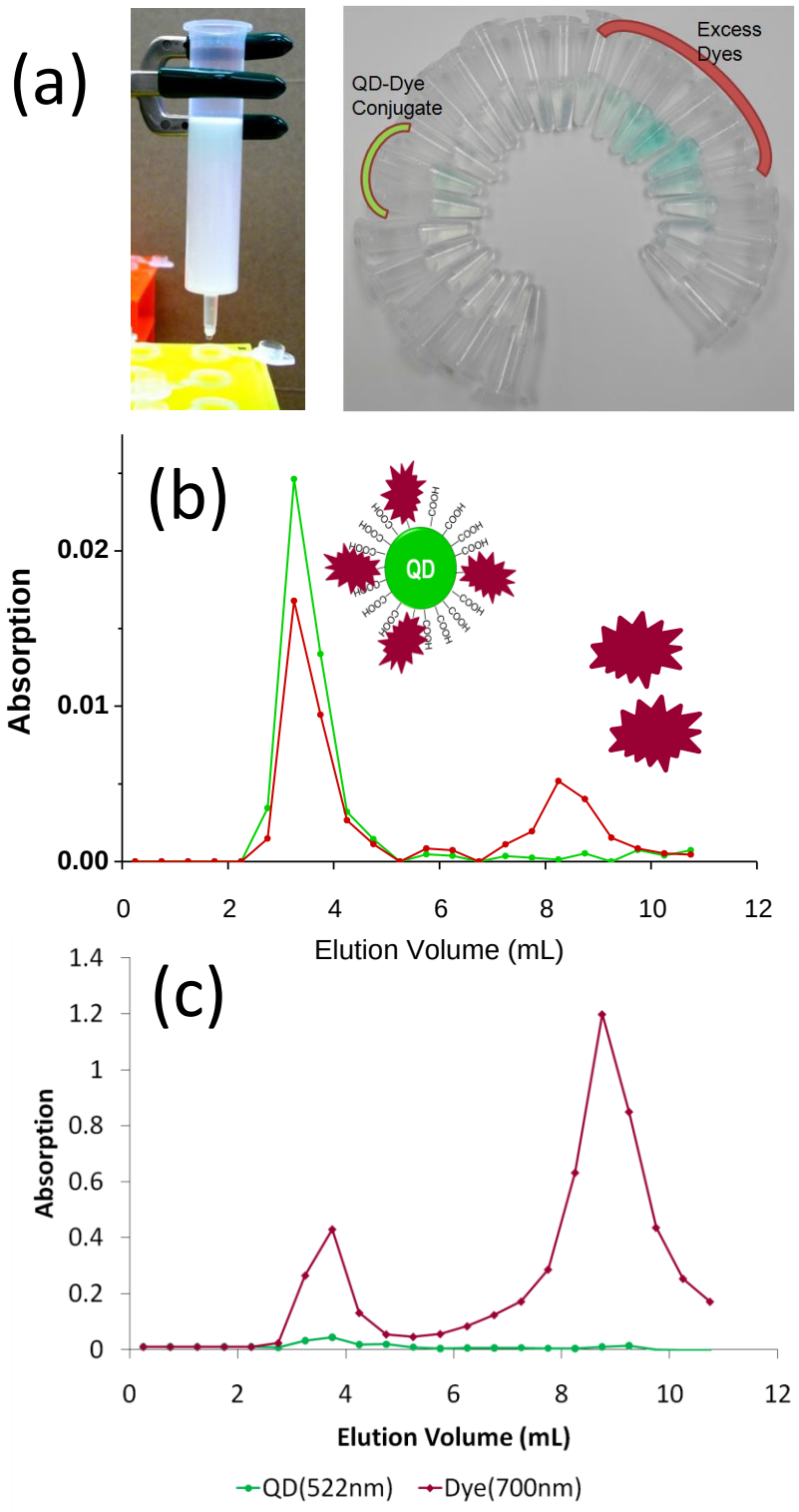
(a)
Excess Dyes
QD-Dye Conjugate
(b)
QD
Absorption
0.02
0.01
0.00
0
2
4
6
8
10
12
Elution Volume (mL)
(c)
Absorption
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
2
4
6
8
10
12
Elution Volume (mL)
QD(522nm)
Dye(700nm)

Figure S4

Probabilistic Aspects of the Hill equation as applied to thiols binding to QDs

The excellent fits of the thiolated dye binding data to the Hill equation was used to analytically determine the cumulative probability and probability density function for dye binding, as previously shown.[1] Using the notation in the main text, the Hill equation is described by equation S1

$$y = \frac{L_{max}x^n}{K^n + x^n} \tag{S1}$$

Where L_{max} is the maximum number of ligands that bind to the QD, K is the relative binding strength and n is the Hill coefficient. y is the number of dyes that actually bound for a given number of dyes added, x. The cumulative probability, P{X}, of dyes binding to their maximum value is therefore given by dividing by L_{max} and rearranging to give equation S2

$$P\{X\} = 1 - \frac{1}{1+\left(\frac{x}{K}\right)^n} \qquad 0 \le X \le L_{max} \tag{S2}$$

Where X is the average number of dyes bound, up to the maximum value, L_{max}. This is plotted for each QD sample in figure S5(a), and is basically just a normalized representation of figure 3(c) in the main text. The probability density function, *PDF{X}*, is the derivative of equation (S2),

$$PDF\{X\} = \frac{dP\{X\}}{dx} = \frac{n\left(\frac{x}{K}\right)^n}{x\left(\left(\frac{x}{K}\right)^n + 1\right)^2} \qquad 0 \le X \le L_{max} \tag{S3}$$

Which is plotted in figure S5(b) as solid lines for each QD sample. The data calculated based on the probability of binding in figure 3(d) in the manuscript are shown as dashed lines for comparison. To ensure the same scaling, each curve of figure 3(d) is divided by L_{max} for plotting in figure S5(b). As can be seen, the analytically-derived PDFs and the calculated probability of binding are very similar, as would be expected. The probability of binding (Figure 3(d) and the dashed lines of figure S5(b)) is calculated using the Hill equation fit parameters to compute the number of dyes attached as a function of the number of dyes added (varying from 0 to 500) and determining the fraction of dyes that bound. The expression based on this calculation is equation (S1) divided by the number of dyes added, x:

$$Fraction\ that\ Bound = \frac{L_{max}x^n}{x(K^n + x^n)} = \frac{L_{max}\left(\frac{x}{K}\right)^n}{x\left(\left(\frac{x}{K}\right)^n + 1\right)} \tag{S4}$$

Comparing equations (S4) and (S3) shows the relationship between fraction bound and the probability density function, and are shown as solid and dashed lines of figure S5(b) (after dividing by the L_{max} scaling parameter). One can see the similarity of the curve shapes, although the PDFs generally overestimate the probability of binding at low concentrations and underestimate it at high concentrations.

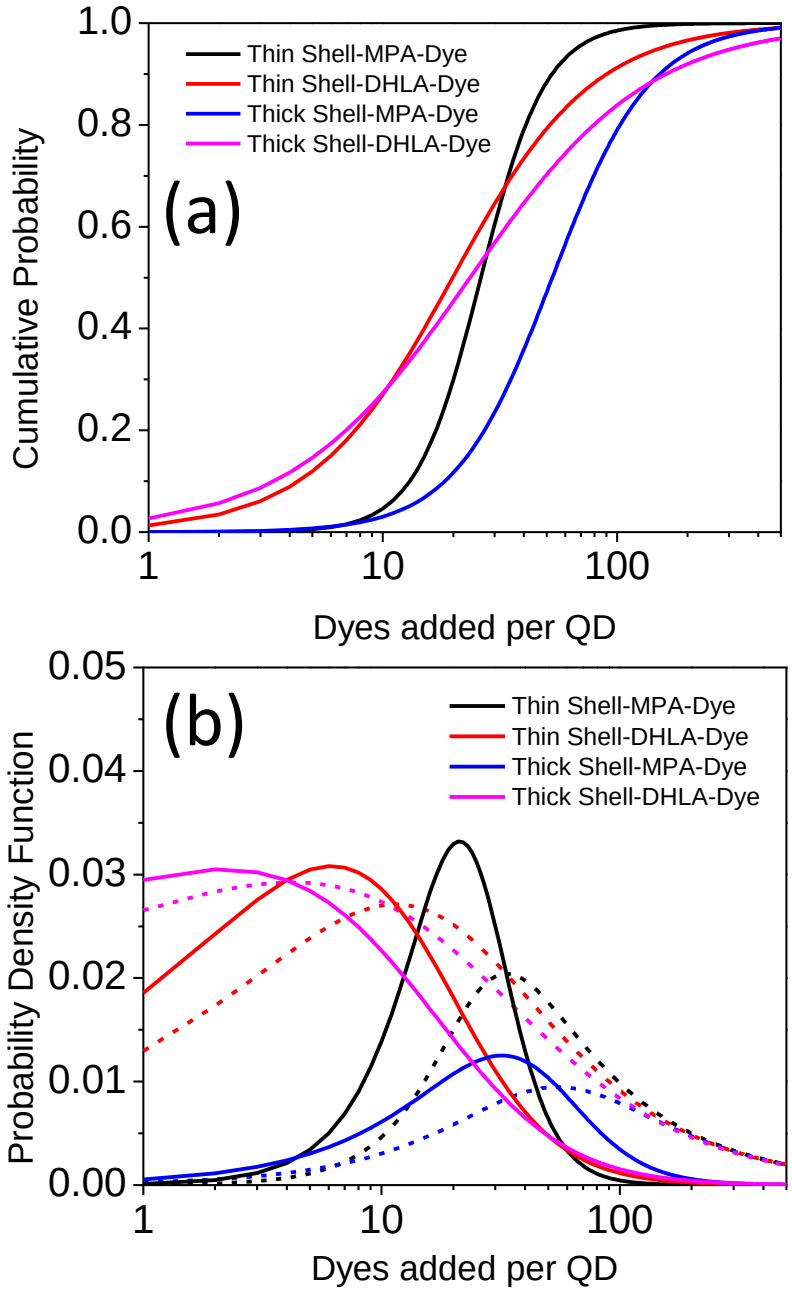

Figure S5

References

1. Goutelle, S.; Maurin, M.; Rougier, F.; Barbaut, X.; Bourguignon, L.; Ducher, M.; Maire, P., The Hill equation: a review of its capabilities in pharmacological modeling. *Fundam. Clin. Pharmacol.* **2008,** *22*, 633-648.